PATENT SPECIFICATION

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(19)

(54) METHOD OF PRINTING

(71) We, REED INTERNATIONAL LIMITED, a British Company of 82, Piccadilly, London, W1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a process for printing a design on a film of a polymer applied to a rigid substrate.

The application of a printed design to a film of a polymer applied to a substrate can transform a single coloured surface into one which is visually attractive and aesthetically pleasing. Furthermore, the application of a design, for example in the form of symbols, may be used to convey information, instructions or warnings. It is known to apply printed designs by a gravure process but this method involves the use of very specialized and expensive apparatus. Moreover difficulties of definition are encountered with the gravure process when multi-colour printing is attempted on a non-absorbent surface such as a film of a polymer applied to a substrate and it is generally desirable to protect a design so printed. Protection may be effected by the application of a clear or translucent film and is desirable so that the printed design is not damaged or removed when the printed article is scratched or rubbed in use.

We have now discovered that a printing process which has hitherto found application primarily in the field of printing textile fibres or fabrics may be used, with advantage, in the application of a design to a film of a particular type of polymer on a rigid substrate.

According to the present invention therefore there is provided a process for printing a design on a film of polyester deposited on a rigid substrate which comprises positioning one surface of a sheet having one or more sublimable dyestuffs printed thereon in the desired design in overlying relation to the polymer film and heating the print sheet to an extent sufficient to cause sublimation of the dyestuffs from the printed sheet and into the polyester film, the said polyester film being formed by curing an unsaturated polyester resin on the said rigid substrate.

On application of heat and, if desired, pressure to the printed sheet (generally referred to as the transfer sheet) the dyestuffs printed thereon vaporize and migrate from the heat source. In the migration process penetration of the polymer film by the dyestuff occurs so that the desired design is not merely produced as a surface layer. Thus scratching or rubbing of the surface of the polymer after the printing process will not cause removal of the design to the extent that the visual impact of the article is in any way effected.

The process according to the invention enables one to eliminate the use of gravure printing in the step of applying a design to a film of polymer on a substrate. In addition to its expense and general inconvenience to use gravure printing has attendant difficulties from an environmental viewpoint. One is working with solutions of dyestuff which are, in general, in an organic solvent so that solvent vapours exist in the workshop. Moreover replenishment of dyeing troughs is regularly required as also is the disposal of waste from spent dye troughs. The disposal of a waste solution of dyestuff can present considerable problems in rendering the waste in a form that will not disturb the ecology of the region surrounding the dyeing plant.

Solutions of dyestuff are not required in the process according to the invention since dyeing is effected with a transfer sheet. As discussed in more detail below the transfer sheet may be a paper sheet and, in these circumstances, a spent transfer sheet may be disposed of in a simple and inexpensive manner for example by burning without any risk of harming the environment.

Furthermore, the process according to the invention enables one to make the printing step the final step in the production of a finished panel of wood, hardboard, metal or the like. Thus final processing

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steps such as the glueing or other affixment of a sheet of printed plastics material to a substrate or the overcoating of design printed on a polymer film with a clear or translucent wear layer are eliminated. Considerable commercial advantages accrue from the process according to the invention since, not only is the time and expense of a further process step or steps eliminated but also one achieves an overall increase in efficiency. Stocks of panels of wood, hardboard, metal etc. coated with a film of polymer on the decorative or wear surface may be stored and then dyed to order quickly and simply so that large stocks of printed panels need not be held while waiting for orders.

The only limitations on the process according to the invention are in the suitability of the substrate and the polymer film to the heating required in the sublimation process. In general temperatures of 100—250°C are required to achieve sublimation and there are advantages in using temperatures in the range of from 150—250°C since, at these higher temperatures, a greater degree of penetration of the polymer film by the dyestuff is achieved.

The sublimation process may conveniently be effected by bringing the transfer sheet and coated panel into intimate contact in a heated press; for example a veneer or laminating press, or by passage through the nip of a set of heated rolls. The coated panel may be cool before positioning the transfer on the polymer film or, alternatively, it may have been heated to a preselected temperature before application of the transfer sheet.

The polyester resin may be applied to the substrate in any convenient manner, for example as a solution or dispersion in an appropriate solvent, and subjected to any necessary curing reactions prior to the printing process. The polymer may be applied in pigmented or unpigmented form so as to achieve an apt base film on the substrate.

The unsaturated polyester resin should contain sufficient residual unsaturation as to enable it to take part in a curing reaction, preferably with an unsaturated monomer. Such polyesters are, in general, formed by reaction of an unsaturated acid (or ester forming derivative thereof) with a polyol although, if desired, the polyol may contribute some or all of the unsaturation to the polyester. The chosen acid and polyol are preferably difunctional or comprise a mixture of polyfunctional materials in which a dibasic acid and dihydric alcohol predominate.

Suitable polyesters may thus be formed by reaction of one or more acids selected from the following group; maleic acid, fumaric acid, itaconic acid, succinic acid or adipic acid or polyester forming derivatives thereof such as the anhydrides (where they exist) with the chosen polyol component. The polyol may, for example, be ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, a butane, pentane or hexane diol, glycerol, pentaerythritol or, if an unsaturated polyol is desired, a butene diol.

The unsaturated polyester so formed may be applied to the substrate together with an unsaturated monomer which, for example, in the case of monomers such as styrene may be the solvent in which the polyester is dissolved. Curing is effected with the aid of the usual accelerators to yield a film of the desired degree of hardness.

The polyester resin may be applied to the rigid substrate together with another polymer which may be included to enhance the properties of the film so formed. In the case of mixtures of polyester resin and another polymer the polyester resin should contribute to at least 50% of the polymer in the film. Suitable polymers for admixture with the polyester are well described in the literature and illustrative of the polymers that may be employed are polyamides (e.g. those formed by reaction of di- and/or triamines with polycarboxylic acids such as the various nylons), polyurethanes (e.g. those prepared by reaction of aliphatic and/or aromatic di- and/or tri-isocyanates with compounds containing active hydrogen atoms present as amino or hydroxyl groups e.g. aromatic amines and polymeric polyols), acrylic polymers (formed, for example, by polymerising monomers derived from acrylic and/or methacrylic acid), polyvinyl resins (formed by polymerisation of monomers containing a vinyl group such as vinyl acetate and/or vinyl chloride), resins formed by reaction of formaldehyde with a compound containing amino groups such as urea or melamine, and cellulosic polymers such as, for example, those based on nitrocellulose.

In the heat transfer process the dyestuff penetrates the polymer film and the degree of penetration is related both to the compatibility of the dyestuff with the polymer and the extent to which the polymer plasticises during heating to allow entry of the sublimed dyestuff. In our experience polyester films formed by curing an unsaturated polyester resin formed by reaction of maleic anhydride with ethylene glycol, diethylene glycol or a polyalkylene ether glycol have been found to possess qualities such as to render them particularly suitable to be dyed by the process according to the invention.

The polymer may be applied to the substrate by any convenient technique such as, for example, roller coating curtain coating, spraying etc. at a rate such as to yield a dry film of 5—50 μ thickness. The polymer may be deposited together with the usual additives such as pigments, plasticisers and accelerators to improve the quality of the film and the deposited film should be subjected to a stoving schedule at a temperature, e.g. 50—150°C, sufficient to complete the formation of the film.

Prior to application of the polymer film the substrate may, if desired, be coated with a primer. This may be desirable in the case of wood surfaces such as plywood, blockboard, chipboard or other manufactured board and certain metal surfaces where the application of a primer may serve to prevent or reduce corrosion or other deterioration of the substrate surface.

The transfer sheet used in the process according to the invention may be prepared in any convenient manner for example by gravure, flexographic, lithographic, typing, letterpress or similar printing of dyestuff in the desired pattern onto a suitable support that yields a relatively smooth surface and is stable at the operating temperature apt for the chosen dyestuff. The support is however preferably paper since this is widely and inexpensively available. The paper may be a kraft coated art paper and is preferably printed with a sufficient thickness of dyestuff so that the transfer sheet may be used in a number of printing operations. A dyestuff layer of 10—20μ thickness is, in our experience sufficient to enable 10—20 printing operations to be successfully affected with the sheet.

A wide variety of variegated designs for example simulated wood designs and the like may be printed on the transfer sheet and sheets of substantial length can be produced for use in the process according to the invention in an economic and efficient manner. It is an advantage of the process according to the invention that there is no need to install expensive printing machinery and the sublimation process may be readily adapted to existing production line techniques such as sanding and painting or lacquering.

The sublimable dyestuff may be an organic or inorganic material. Organic dyestuffs are preferred since, in general, these are more readily sublimable than are inorganic materials. Moreover organic dyestuffs are more easily presented in a form suitable for application to the transfer sheet. A wide variety of sublimable organic dyestuffs have been described in the art and suitable materials for use in the process according to the invention are the anthraquinone dyestuffs such as hydroxy and/or amino substituted anthraquinones; azo dyestuffs, in particular mono- and di-azo compounds wherein the azo group(s) bridge two aromatic rings, which may be substituted by amino, hydroxy and/or nitro groups; phthalocyanine dyestuffs; azomethine dyestuffs; and stilbene dyestuffs. Nitro and nitroso groups are known chromophores and it will be understood that any of the aforesaid dyestuffs may be substituted by one or more of these groups. In formulating a multicolour transfer sheet care should be taken to ensure that the sublimation temperatures of the dyestuffs are sufficiently similar as to enable both dyestuffs to sublime into the polymer film at the chosen operating temperature to yield clear, sharply defined images. The dyestuffs may be formulated as a solution or dispersion in an aqueous or organic solvent containing a binder and applied to the transfer sheet by any of the usual printing techniques.

The invention is further described in the following examples which are given by way of illustration only. Parts referred to are, unless otherwise stated, parts by weight. The words Roskydal and Aerosil as used herein are Registered Trade Marks.

Example 1

The process of the invention was used to apply a floral design to a kitchen cabinet door comprising a chipboard core bonded onto both faces of which was a paper foil impregnated with a melamine resin. The door was coated on one side (by means of a roller coater) with an active primer to yield a dry film thickness of 20 μ. The active primer was based on the following formulation:

	parts
Wax- and styrene-free unsaturated polyester resin (75% solution in butyl acetate) (1)	30.00
Nitrocellulose DHX 3/5 (70% in isopropanol)	14.00
Methyl isobutyl ketone	12.50
Isobutyl acetate	10.00
Ethyl acetate	10.00
Cyclohexanone peroxide (90% in water)	14.00
Methyl ethyl ketone peroxide (40% in dibutyl phthalate)	9.50

(1) Commercially available as Roskydal W15.

After drying for two minutes a solution of a polyester resin in styrene was applied to yield a dry film thickness of 400 μ. The

coating applied was based on the following formulation:

	parts
Titanium dioxide	9.00
Silica suspending agent (Aerosil 300)	0.25
Air drying wax-free unsaturated polyester resin (2)	20.60
Air drying wax-free unsaturated polyester resin (3)	53.50
Ethylene glycol dimethacrylate	15.50
Cobalt fatty acid accelerator	0.02
t-Butyl catechol (1% in styrene)	0.05
Styrene	1.08

(2) Commercially available as Roskydal 500A

(3) Commercially available as Roskydal 550

The film of polyester so deposited was cured on a production line utilising 5 minutes convection heating rising from 20 to 120°C, followed by 1 minute exposure to infrared radiation. After cooling, the surface of the polyester lacquer was sanded flat with fine abrasive paper and subsequently burnished to a high gloss.

The polyester film was thus completed and in a form whereby the door panel could be stored until an order for a printed panel was received or sold when an order for a plain white panel was placed. A transfer sheet onto which a multicolour floral design had been printed was laid printed face downwards on the polyester lacquer surface, and transfer sheet and door panel were placed in a heated press. A pressure of 2 lbs. per square inch was applied with the platten (in contact with the underside of the transfer sheet) at a temperature of 200°C and allowed to dwell there for 7 seconds. Almost immediately the transfer sheet was stripped off and with no further treatment the door was ready for fitting into a kitchen cabinet.

Example 2

In a manner analogous to that described in Example 1 a multicolour abstract design was applied to a substrate coated with the active primer used in Example 1 but with a white polyester lacquer of different composition. In this case the active primer was applied by curtain coater at a film weight of 60 grams per square metre and allowed to dry for 2 hours. The polyester lacquer in this example was based on the following formulation:

	parts
Unsaturated polyester resin (65% in Styrene) (4)	75.00
Titanium dioxide	7.50
Silica suspending agent (Aerosil 300)	0.42
Styrene	15.00
Cobalt fatty acid accelerator in toluene (2.2% metal content)	1.14
Paraffin wax (50.52°C) (10% in toluene)	0.94

(4) Commercially available as Roskydal W9

The lacquer was applied by curtain coater at a film weight of 500 grams per square metre and allowed to cure at a temperature of 20°C for 16 hours.

During the curing process the wax migrated to the surface of the lacquer film and this surface layer was completely removed at the end of the curing period by sanding with 320 grade abrasive paper. The resultant surface was further sanded with 400 grade abrasive paper and subsequently burnished to a high gloss. After removal of the transfer backing paper, the door was ready for fitting into a cabinet with no further treatment.

WHAT WE CLAIM IS:—

1. A process for printing a design on a film of polyester deposited on a rigid substrate which comprises positioning one surface of a sheet having one or more sublimable dye-stuffs printed thereon in the desired design in overlying relation to the polymer film and heating the printed sheet to an extent sufficient to cause sublimation of the dyestuffs from the printed sheet and into the polyester film, the said polyester film being formed by curing an unsaturated polyester resin on the said rigid substrate.

2. A process as claimed in Claim 1 wherein heating is effected to a temperature of from 100 to 250°C.

3. A process as claimed in Claim 1 or Claim 2 wherein the polyester film is formed from a mixture of the said unsaturated polyester resin with not more than 50% of another polymer.

4. A process as claimed in any of the preceding Claims wherein the polyester coated rigid substrate is heated to a preselected temperature before application of the transfer sheet thereto.

5. A process as claimed in any of the preceding Claims wherein the unsaturated polyester film is formed by reaction of an unsaturated acid or an ester forming derivative thereof with a polyol.

6. A process as claimed in Claim 5 wherein the unsaturated polyester resin is formed by reaction of maleic anhydride

with ethylene glycol, diethylene glycol or a polyalkylene ether glycol.

7. A process as claimed in any of the preceding Claims wherein the unsaturated polyester resin is applied at a rate such as to yield a dry film of 5—50 μ thickness.

8. A process as claimed in Claim 1 substantially as described herein.

9. A process as claimed in Claim 1 substantially as described herein with reference to the Examples.

10. A polyester coated rigid substrate having a design printed thereon by a process as claimed in any of the preceding Claims.

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